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The Raman spectrum of cyclohexyl benzene

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(Plate—9)

The Raman spectrum of cyclohexyl benzene has been studied in the present investigation. About fourteen lines have been recorded. The Raman and infrared spectra of cyclohexyl benzene are discussed in relation with those of benzene and cyclohexane.

Introduction

The Raman spectra of benzene and cyclohexane are well known. The cyclohexyl benzene is also known as phenyl cyclohexane or hexahydro-diphenyl. The structure can be represented by the substitution of one of the hydrogen atoms in cyclohexane by a phenyl ring. The infrared spectrum of cyclohexyl benzene is already reported by the author (1962) and it was thought necessary to study the Raman spectrum of the molecule and find the Raman frequencies and discuss the two spectra, since, no previous work has been done on this molecule in this direction.

Experimental

The Raman spectrum of cyclohexyl benzene was photographed on a three prism Steinheil spectrograph. The Raman source of Steinheil described previously by the author (1959) was used in the present investigation. Experimental details are now well known. An exposure of eight hours with this source was necessary to bring out the details in the spectrum (figure 1). The frequencies of the Raman lines of cyclohexyl benzene are given in table 2 with intensities visually estimated, the strongest line being estimated as ten.

Only principal vibration frequencies of cyclohexyl benzene along with corresponding ones for benzene and cyclohexane are given in the above table. The frequencies are taken from Infrared and Molecular Spectra by Herzberg.

Discussion

The normal vibrations of the benzene molecule have been worked out by Wilson (1934) who has ascribed it to twenty distinct fundamental frequencies. The benzene molecule is well known to have the shape of a regular plane hexagon and belongs to the symmetry group D_{6h}. This has been dealt with both theoretically and experimentally by Ingold (1936) and his coworkers. Of the twenty fundamentals of benzene seven (five degenerate and two non degenerate) are

TABLE 1. Principal infrared frequencies of cyclohexane, cyclohexyl benzene and benzene

cyclohexane	cyclohexyl benzene	benzene
	3039 s	3021 s
		(3044) (Raman)
2933 vvs	2932 vs	—
2841 (?)s	2865* vs	—
	1607* s	(1606) inactive in benzene
	1588 s	(1587) inactive in benzene
	1495 vs	1479 vs
1449 vvs	1449* vs	—
	1177 m	1178 m
	1068	
	1029*b	1036 vvs
1016 mw	1005	
	996*	993
	884	
861 vvs	863 ms	
	829* m	847
	778*	—
	753	—
	696 vvs	680 s

s-strong, vs-very strong, vvs-very very strong m-medium and mw-medium weak *common to both Raman and infrared.

TABLE 2. Raman frequencies in cm^{-1} of cyclohexyl benzene

cyclohexane	cyclohexyl benzene	benzene	substituent
	3068 (5)	3061	
2937	2945 (5)		
2853	2865 (6)		
	2795 (6)		—C— of cyclohexyl benzene (H)
	1607 (5)	1606	
1442	1442 (5)		
	1203 (1)	1178	C—C substituent
1029	1030 (2)		
	999 (10)	991	
	826 (1)	847	
	778 (3)		
	624 (3)	606	
	280 (3)		C—C substituent in plane
	147 (2)		C—C substituent out of plane

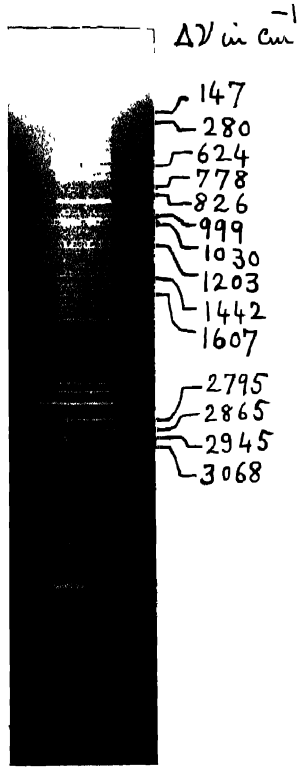

Figure 1. Raman spectrum of cyclohexylbenzene.

allowed in the Raman effect and four fundamentals (three degenerate and one non-degenerate) are allowed in the infrared. Because of the centre of symmetry, fundamentals which are allowed in the Raman effect are forbidden in the infrared and the converse is true.

In cyclohexyl benzene due to the substitution of C_6H_{11} in place of one of the H atoms of benzene, the symmetry D_{6h} is reduced to C_{2v}, if we assume the cyclohexyl group to behave as a single atom. The transformation properties and the selection rules of the various symmetry types of this point group and the number of vibrations of the molecule belonging to each symmetry type are well-known (Sponer 1942). Cyclohexyl benzene may be considered as a monosubstituted benzene.

Infrared spectrum

The principal vibration frequencies of cyclohexyl benzene (Bapat 1962) along with corresponding ones for benzene and cyclohexane are tabulated in table 1. Under the C_{2v} group all frequencies except the A_2 frequencies are allowed.

In the C—H stretching region a band near 3039 cm^{-1} obviously corresponds to one of the CH stretching bands of the benzene group. Since the symmetry is reduced it is likely that 3044 cm^{-1} of Raman spectrum of benzene may be the one which corresponds to 3030 cm^{-1} in the present case. 2932 and 2865 cm^{-1} bands arise from the CH stretching of the CH_2 group of cyclohexyl part and have been shown to be as such. The prominent band 1607 cm^{-1} in the present case arises from benzene part and corresponds to either of the 1606 cm^{-1}, 1596 cm^{-1} Fermi doublet in benzene arising from C—C stretching. The shoulder at 1588 cm^{-1} may correspond to other component; the Raman Spectrum, however does not show a line corresponding to this The 1495 cm^{-1} band here corresponds to 1479 cm^{-1}, C–C stretching band of benzene, whereas the strong band at 1449 cm^{-1} corresponds to strong band at 1449 cm^{-1} in cyclohexane corrsponding to CH_2 bending vibration. 1177 and 1029 cm^{-1} in the present case correspond to inplane hydrogen bending vibration of benzene. The strong band at 996 cm^{-1} corresponds to symmetric stretching of benzene ring 829 and 696 cm^{-1} in the present case correspond to 847 and 680 cm^{-1} out of plane hydrogen bending vibrations of benzene. A very prominent band at 863 cm^{-1}in the present case corresponds to out of plane hydrogen bending of the cyclohexane group.

It is thus apparent that the whole spectrum can be conveniently divided into more or less distinct groups of bands arising from the cyclohexane and phenyl part It is observed that the frequencies are not markedly perturbed by the substituent in either part, principally because one is aromatic nucleus with aromatic C—H bonds, whereas the other is an aliphatic saturated ring with cyclic

methylene groups. The two have very distinct characteristic spectra. It is further observed that there are a number of frequencies which are common to infrared and Raman spectra and that cyclohexyl substitution markedly relaxes the selection rules of D_{6h} group of benzene. The analysis of only the prominent bands is given here. The complete analysis shows that the spectrum can be easily accounted for as a superposition of two spectra when account is taken of the large number of fundamentals.

Raman spectrum

All the frequencies observed in Raman spectrum of cyclohexyl benzene are recorded in table 2. The table also records the relevant Raman frequencies of benzene and cyclohexane. It is observed that here again all the fundamentals active in the Raman spectrum of benzene are observed.

In the Raman spectrum of benzene the frequency 991 cm^{-1} appears with great intensity. This can be correlated with the frequency 999 cm^{-1} present very strongly in cyclohexyl benzene. This may be assigned as corresponding to 992 a_{1g} breathing vibration of benzene. It has been observed that the monosubstituted benzenes have a very characteristic Raman band near 620 cm^{-1} and this has been justified in the present case by the frequency 624 cm^{-1} present in the Raman spectrum of cyclohexyl benzene and corresponds to 606 cm^{-1} of benzene. The frequency 1607 cm^{-1} in cyclohexyl benzene can be correlated with the frequency 1606 cm^{-1} in benzene. This is one of Fermi doublet at 1606 and 1586 cm^{-1} which is prominent in the Raman spectrum of benzene. It is worth noting that only one component of the doublet appears prominently. Again the frequency 2945 cm^{-1} in cyclohexyl benzene can be correlated with the frequency 2937 cm^{-1} in cyclohexane. In the Raman spectrum of benzene there is a strong band at 3061 cm^{-1} due to the C—H stretching vibration while a similar band is present at 3068 cm^{-1} in the Raman spectrum of cyclohexyl benzene.

A characteristic band at 2795 cm^{-1} with apparently no analogue in either case arises from C—H tertiary group at the substituted carbon of cyclohexyl ring. Other frequencies in the Raman spectrum correspond to cyclohexane part. Apart from 2945, 2865 cm^{-1} bands which correspond to symmetric and asymmetric stretching vibration of CH_2 group, 1442 cm^{-1} corresponding to CH_2 bending is also shown in cyclohexyl benzene.

In the Raman spectrum the bands 1203, 280 and 147 cm^{-1} find no analogue in the spectra of either constituent. Apparently because of a monosubstitution, there should be one (phenyl) C—C (substituting) stretching and one each inplane and out of plane bending vibration; 1203 cm^{-1} possibly does not correspond to 1178 of benzene because infrared band at 1177 cm^{-1} has been assigned to this mode. Thus 1203 cm^{-1} possibly represents C—C stretching

and 280 and 147 in plane and out of plane substituent bending vibrations. It is important to note that all substituent modes are predominantly Raman active because of close similarity of substituents. Since both phenyl as well as cyclohexane do not have such low frequency vibrations in the range of 280 or 147 and because of the large mass of substituent, the analysis of these is fairly correct.

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